

# Metal/Semi-Conductivity and Antiferromagnetic Ordering of Fe(III) d spins in (Benzotetrathiafulvalenothioquinone-1,3-dithiolemethide)<sub>2</sub>•FeBr<sub>4</sub>

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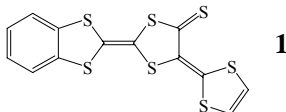
## Abstract

A new donor molecule, benzotetrathiafulvalenothioquinone-1,3-dithiolemethide (**1**) was prepared and electrochemically oxidized in the presence of NEt<sub>4</sub>MX<sub>4</sub> (M = Fe, Ga; X = Cl, Br) to give its charge transfer (CT) salts with MX<sub>4</sub><sup>-</sup> ions (**1**<sub>2</sub>•FeCl<sub>4</sub>, **1**<sub>2</sub>•GaCl<sub>4</sub>, **1**<sub>2</sub>•FeBr<sub>4</sub>, **1**<sub>2</sub>•GaBr<sub>4</sub>). These CT salts exhibited considerably high electrical conductivities of 16 - 33 S cm<sup>-1</sup> at room temperature. Their electrical conducting properties were metallic above 200 K, but below this temperature became semiconducting behavior with very small activation energies of 4 - 27 meV. Both of the Fe(III) (*S* = 5/2) d spins of FeCl<sub>4</sub><sup>-</sup> and FeBr<sub>4</sub><sup>-</sup> ions were subjected to antiferromagnetic interaction, and there was a sign of antiferromagnetic ordering at around 8 K in the FeBr<sub>4</sub><sup>-</sup> salt.

## 1. Introduction

Current interest continues to be directed toward molecular/organic magnetic conductors, in which conducting  $\pi$  electrons and local d spins are expected to significantly interact with each other so as to produce unusual electrical conducting and/or magnetic properties. Especially, a great deal of progress has been made so far in several CT salts of  $\pi$  donor molecules with magnetic-metal counteranions, from which paramagnetic superconductivity [1], antiferromagnetic superconductivity [2], metallic ferromagnetism [3] and field-induced ferromagnetic superconductivity [4] emerged. However, simultaneous appearance of novel magnetism and electrical conductivity in the CT salts is not always a result of the interaction between the conducting  $\pi$  electrons and the local d spins involved there. Generally, the  $\pi$ /d interaction is scarcely very weak in all the CT salts except for a  $\lambda$ -type of CT salt of bis(ethylenedithio)tetrathiafulvalene (BETS) with FeCl<sub>4</sub><sup>-</sup> ion [5], in which significant  $\pi$ /d interaction, however, begins to occur only at low temperatures.

Under the circumstances it is now desired to urgently search for donor molecules other than BETS, which give new salts with magnetic-metal counteranions exhibiting much more increased  $\pi$ /d interaction, by which unprecedented electrical conducting and/or magnetic properties might come out. Very recently, we observed ferromagnetic ordering of Fe(III) d spins of FeBr<sub>4</sub><sup>-</sup> ions near 1 K through the interaction with the  $\pi$  spins developed on the donor columns in the CT salt of ethylenedithiotetrathiafulvalenothioquinone-1,3-dithiolemethide with a magnetic FeBr<sub>4</sub><sup>-</sup> ion [6]. However, this CT salt has problems of metal-to-semiconductor transition near 170 K and very weak  $\pi$ -d interaction. Now, we had much interest in a new donor molecule, **1**, which has a planar and  $\pi$ -donating benzo group in place of an ethylenedithio group. Here are reported the synthesis of CT salts of **1** with Fe(Ga)Cl<sub>4</sub><sup>-</sup> and Fe(Ga)Br<sub>4</sub><sup>-</sup> ions, and their crystal structures, and electrical conducting and magnetic properties.



## 2. Experimental

According to the previous procedure, **1** was prepared using bis-(cyanoethylthio)benzotetrathiafulvalene as a starting material: overall yield 35%; mp 251 - 252 °C (dec). The **1**<sub>2</sub>•MX<sub>4</sub> salts were obtained by an electrochemical oxidation of a chlorobenzene/ethanol (9:1, v:v) solution containing **1** (5 mg) and NEt<sub>4</sub>MX<sub>4</sub> (40 - 80 mg) in a conventional H-shaped cell with Pt electrode at 293 K over 10 days at a constant current of 0.3  $\mu$ A. X-Ray diffraction data were collected at 297 K on a Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite-monochromated Mo-K $\alpha$  radiation or on a Rigaku AFC-8 Mercury CCD diffractometer with a confocal X-ray mirror system. Their crystal data were as follows. **1**<sub>2</sub>•FeCl<sub>4</sub>: monoclinic, space group *P*2<sub>1</sub>/m, *a* = 7.0447(9), *b* = 34.734(3), *c* = 7.622(1) Å,  $\beta$  = 74.020(3)°, *V* = 1793.0(4) Å<sup>3</sup>, *R*<sub>1</sub> = 0.041. **1**<sub>2</sub>•GaCl<sub>4</sub>: monoclinic, space group *P*2<sub>1</sub>/m, *a* = 7.063(1), *b* = 34.578(7), *c* = 7.607(2) Å,  $\beta$  = 73.83(1)°, *V* = 1784.4(6) Å<sup>3</sup>, *R*<sub>1</sub> = 0.048.

**1**<sub>2</sub>•FeBr<sub>4</sub>: monoclinic, space group *P*2<sub>1</sub>/m, *a* = 7.063(3), *b* = 35.514(12), *c* = 7.661(3) Å,  $\beta$  = 105.673(1)°, *V* = 1850.3(11) Å<sup>3</sup>, *R*<sub>1</sub> = 0.050. **1**<sub>2</sub>•GaBr<sub>4</sub>: monoclinic, space group *P*2<sub>1</sub>/m, *a* = 7.073(2), *b* = 35.602(7), *c* = 7.661(2) Å,  $\beta$  = 106.0624(10)°, *V* = 1853.8(7) Å<sup>3</sup>, *R*<sub>1</sub> = 0.043. Electrical conductivity measurement was performed on the single crystals using a four-probe method. The static magnetic susceptibility was measured between 1.8 and 300 K using the microcrystals of **1**<sub>2</sub>•FeCl<sub>4</sub> and **1**<sub>2</sub>•FeBr<sub>4</sub> under an applied field of 1 kOe on a SQUID susceptometer (MPMSXL, Quantum Design).

## 3. Results and Discussion

The crystal structures of **1**<sub>2</sub>•FeCl<sub>4</sub> and **1**<sub>2</sub>•FeBr<sub>4</sub> projected down to *bc* and *ab* planes are shown in Fig. 1 and Fig. 2, respectively. The GaCl<sub>4</sub><sup>-</sup> and GaBr<sub>4</sub><sup>-</sup> salts have almost the same crystal structures to those of the corresponding FeCl<sub>4</sub><sup>-</sup> and FeBr<sub>4</sub><sup>-</sup> salts. In both of **1**<sub>2</sub>•Fe(Ga)Cl<sub>4</sub> and **1**<sub>2</sub>•Fe(Ga)Br<sub>4</sub>, **1** molecules are stacked in almost the same manner to form a one-dimensional column, in which the neighboring **1** molecules have comparatively effective overlap and the interplanar distances are almost equal (3.49 - 3.50 Å) and comparable to “ $\pi$ -cloud thickness”. In addition, there are several contacts through the S atoms of the tetrathiaethylene moieties and C=S groups of **1** molecules between the neighboring columns. It should be noted that the Fe(Ga)Cl<sub>4</sub><sup>-</sup> and Fe(Ga)Br<sub>4</sub><sup>-</sup> salts have almost the same **1**-stacked column and layer structures in spite of different sizes of Fe(Ga)Cl<sub>4</sub><sup>-</sup> and Fe(Ga)Br<sub>4</sub><sup>-</sup> ions, which only bring about marked change in the distance between the layers (4.55 - 4.59 Å for **1**<sub>2</sub>•Fe(Ga)Cl<sub>4</sub>, and 5.00 - 5.05 Å for **1**<sub>2</sub>•Fe(Ga)Br<sub>4</sub>).

The Fe(Ga)Cl<sub>4</sub><sup>-</sup> and Fe(Ga)Br<sub>4</sub><sup>-</sup> ions are arranged in a square lattice between the neighboring layers of **1** molecules. The Cl...Cl and Br...Br contact distances between the neighboring Fe(Ga)Cl<sub>4</sub><sup>-</sup> ions are 4.28 and 4.38 Å, and between the neighboring Fe(Ga)Br<sub>4</sub><sup>-</sup> ions are 4.10 and 4.26 Å, respectively, which are longer than the sum of van der Waals radii (vwrs) of two Cl atoms (3.60 Å) and two Br atoms (3.90 Å). The Cl and Br atoms of these ions have also contacts with the S atoms of 1,3-dithiole groups in **1**. The Cl...S contact distances are 3.34 and 3.76 Å, and one is shorter but the other is longer than the sum of vwrs of Cl and S atoms

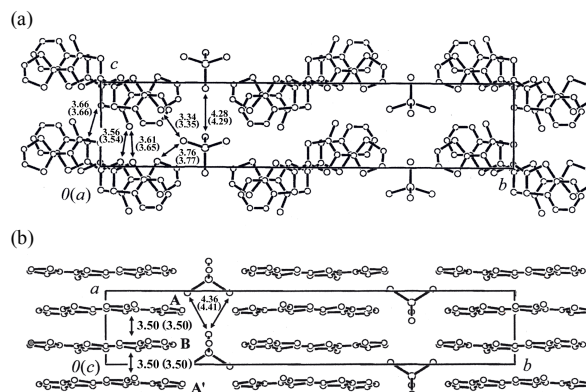


Fig. 1. The crystal structure of **1**<sub>2</sub>•FeCl<sub>4</sub> projected to (a) *bc* and (b) *ab* planes

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| 1. REPORT DATE<br><b>JUL 2004</b>  |                                    | 2. REPORT TYPE<br><b>N/A</b>        |  | 3. DATES COVERED<br><b>-</b>    |                                 |
| 4. TITLE AND SUBTITLE<br><b>Metal/Semi-Conductivity and Antiferromagnetic Ordering of Fe(III) d spins in (Benzotetrathiafulvalenothioquinone-1,3-dithiolemethide)2FeBr4</b>  |                                    |                                     | 5a. CONTRACT NUMBER                      |                                 |                                 |
|  |                                    |                                     | 5b. GRANT NUMBER                         |                                 |                                 |
|  |                                    |                                     | 5c. PROGRAM ELEMENT NUMBER               |                                 |                                 |
| 6. AUTHOR(S)   |                                    |                                     | 5d. PROJECT NUMBER                       |                                 |                                 |
|  |                                    |                                     | 5e. TASK NUMBER                          |                                 |                                 |
|  |                                    |                                     | 5f. WORK UNIT NUMBER                     |                                 |                                 |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br><b>AOARD/AFOSR Unit 45002 APO AP 96337-5002</b>  |                                    |                                     | 8. PERFORMING ORGANIZATION REPORT NUMBER |                                 |                                 |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  |                                    |                                     | 10. SPONSOR/MONITOR'S ACRONYM(S)         |                                 |                                 |
|  |                                    |                                     | 11. SPONSOR/MONITOR'S REPORT NUMBER(S)   |                                 |                                 |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT<br><b>Approved for public release, distribution unlimited</b>  |                                    |                                     |  |                                 |                                 |
| 13. SUPPLEMENTARY NOTES<br><b>Proceedings of the International Conference for the Science and Technology of Synthetic Metals (ICSM 2004). Held in New South Wales, Australia on Jun 28- July 2 2004. Copyrighted: Government Purpose Rights License. See also ADM001811.</b>   |                                    |                                     |  |                                 |                                 |
| 14. ABSTRACT   |                                    |                                     |  |                                 |                                 |
| 15. SUBJECT TERMS  |                                    |                                     |  |                                 |                                 |
| 16. SECURITY CLASSIFICATION OF:  |                                    |                                     | 17. LIMITATION OF ABSTRACT<br><b>UU</b>  | 18. NUMBER OF PAGES<br><b>2</b> | 19a. NAME OF RESPONSIBLE PERSON |
| a. REPORT<br><b>unclassified</b>   | b. ABSTRACT<br><b>unclassified</b> | c. THIS PAGE<br><b>unclassified</b> |  |                                 |                                 |

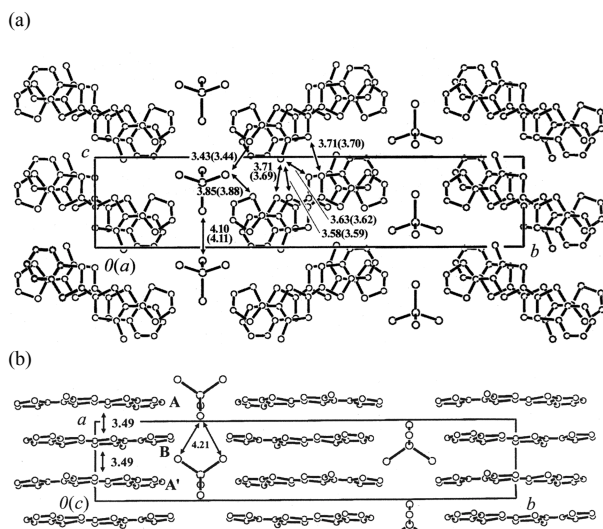


Fig. 2. The crystal structure of  $1_2 \cdot \text{FeBr}_4$  projected to (a)  $bc$  and (b)  $ab$  planes

(3.65 Å). On the other hand, the  $\text{Br} \cdots \text{S}$  contacts have distances of 3.43 and 3.85 Å, and one is shorter than the sum of  $r_{\text{Br}}$  and  $r_{\text{S}}$  atoms (3.80 Å), and the other is comparable to the value.

Electrical conductivity results of  $1_2 \cdot \text{FeCl}_4$ ,  $1_2 \cdot \text{GaCl}_4$ ,  $1_2 \cdot \text{FeBr}_4$  and  $1_2 \cdot \text{GaBr}_4$  are summarized in Table 1. As expected from the uniform and effective stacking of **1**'s with one positive charge per two molecules, all the CT salts exhibited good electrical conductivities ( $\sigma$ 's) at room temperature ( $\sigma_{\text{RT}}$ 's), which are the highest among CT salts of several derivatives of **1** so far obtained. From the temperature dependence of  $\sigma$ , metallic behavior was only recognized in the higher temperature region than 208 - 270 K, and below the temperature it changed to be semiconducting with very small activation energy of < 30 meV. Supposedly, this metal-to-semiconductor transition occurring at considerably high temperatures reflects one-dimensional character of the **1**-stacked columns.

Table 1. Electrical conducting properties of  $1_2 \cdot \text{Fe}(\text{Ga})\text{Cl}_4$  and  $1_2 \cdot \text{Fe}(\text{Ga})\text{Br}_4$ .

|                           | $\sigma_{\text{RT}}$<br>( $\text{S cm}^{-1}$ ) | M - I transition<br>temperature<br>(K) | activation<br>energy<br>(meV) |
|---------------------------|--|--|-------------------------------|
| $1_2 \cdot \text{FeCl}_4$ | 19   | 232                                    | 5 - 18                        |
| $1_2 \cdot \text{GaCl}_4$ | 18   | 208                                    | 8 - 27                        |
| $1_2 \cdot \text{FeBr}_4$ | 33   | 268                                    | 4 - 18                        |
| $1_2 \cdot \text{GaBr}_4$ | 16   | 270                                    | 13                            |

The temperature dependence of paramagnetic susceptibility ( $\chi_p$ ) was investigated in the temperature range of 1.8 - 300 K for  $1_2 \cdot \text{FeCl}_4$  and  $1_2 \cdot \text{FeBr}_4$ . As shown in Figure 3, there is marked difference in the  $\chi_p$  -  $T$  behavior between the two salts. Thus, for  $1_2 \cdot \text{FeCl}_4$  the  $\chi_p$  simply increased with lowering the temperature from 300 K. The  $\chi_p$  -  $T$  behavior can be well reproduced by giving  $C = 4.54 \text{ emu K mol}^{-1}$ ,  $\theta = -4.3 \text{ K}$  to an equation of  $\chi_p = C/(T - \theta)$ , where  $C$  is Curie constant,  $\theta$  Weiss temperature. The  $C$  obtained is very close to the value (4.46  $\text{emu K mol}^{-1}$ ) calculated as  $\text{Fe(III)}$  d spin entity with  $S = 5/2$  and  $g = 2.0179$ . The  $\theta$  value is very small and negative, indicating that very weak antiferromagnetic interaction preferentially occurs between the  $\text{Fe(III)}$  d spins of  $\text{FeCl}_4^-$  ions. On the other hand, for  $1_2 \cdot \text{FeBr}_4$  the  $\chi_p$  also increased with lowering the temperature from 300 K, but the increasing degree was very small compared to that for  $1_2 \cdot \text{FeCl}_4$ . In addition, a peak appeared at ca. 8 K and below the temperature the  $\chi_p$  reversely decreased with

lowering the temperature. In the temperature range of 8 - 300 K the  $\chi_p$  well obeyed an equation as above with  $C = 4.56 \text{ emu K mol}^{-1}$ ,  $\theta = -16.1 \text{ K}$ . Judging from this large and negative  $\theta$  value, the interaction between the  $\text{Fe(III)}$  d spins of  $\text{FeBr}_4^-$  ions is fairly stronger than that of the  $\text{FeCl}_4^-$  salt. This can be well understood by considering the X-ray structure result as above that much closer contacts occur between the Br atom of  $\text{FeBr}_4^-$  ion and the S atoms in the 1,3-dithiole rings. Supposedly, at low temperatures such a one-dimensional antiferromagnetic interaction can furthermore extend to become two- and/or three-dimensional, eventually giving rise to antiferromagnetic ordering of the  $\text{Fe(III)}$  d spins of  $\text{FeBr}_4^-$  ions below 8 K.

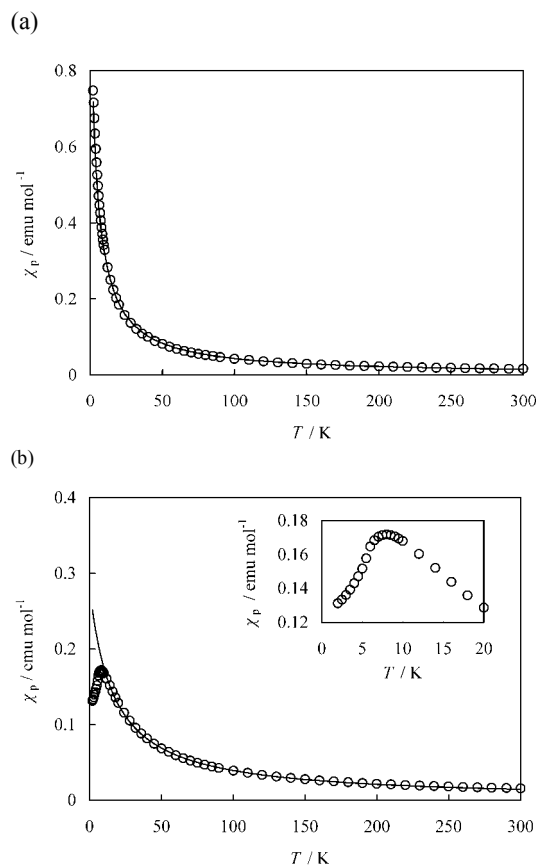


Fig. 3. Temperature dependence of  $\chi_p$  in (a)  $1_2 \cdot \text{FeCl}_4$  and (b)  $1_2 \cdot \text{FeBr}_4$ .

## 4. Conclusions

It was shown that **1** is superior to its related donor molecules in the formation of uniform and effective conducting columns and also in such stronger  $\pi$ -d interaction with a magnetic  $\text{FeBr}_4^-$  ion as to possibly bring about antiferromagnetic ordering near 8 K due to the conducting  $\pi$  electrons or the  $\pi$  spins on the **1**-stacked columns.

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